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THERMAL DECOMPOSITION OF SOME LINEAR

PERFLUOROALKANES IN AN INCONEL BOMB

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SUMMARY

While there is some interest in the utilization of the chemically stable perfluorocarbons at higher temperatures, insufficient information is available concerning the thermal decomposition of perfluorocarbons in general. Of particular interest is information concerning the pyrolysis of three representative linear perfluoroalkanes: (1) perfluoropropane, (2) perfluoroethane, and (3) carbon tetrafluoride.

Perfluoropropane was heated in an Inconel bomb between 663° and 1033° C. Up to about 750° C the products were, essentially, 1 mole of perfluoroethane, some perfluoroisobutene, and some polymeric fluorocarbon per mole of decomposed perfluoropropane. The rates of the decomposition reaction were observed between 670° and 719° C. The rate equation was calculated to be as follows:

$$k = 2 \times 10^{14} e^{-80,000/RT} \qquad (sec^{-1})$$

where k is the specific reaction-rate constant, R is the universal gas constant, and T is temperature.

Perfluoroethane was heated in the Inconel bomb between 746° and 990° C. Up to 824° C, 2 moles of polymeric fluorocarbon and 1 mole of metal fluoride per mole of decomposed perfluoroethane were produced. The following rate equation was calculated from the data observed between 747° and 807° C:

$$k = 3 \times 10^{7} e^{-53,000/RT} \qquad (sec^{-1})$$

Finally, carbon tetrafluoride was heated between 936° and 1090° C. Only a polymeric fluorocarbon and a metal fluoride were obtained. The rates of the decomposition were observed between 930° and 990° C. The following rate equation was calculated:

$$k = 4 \times 10^{13} e^{-96,000/RT} \qquad (sec^{-1})$$

INTRODUCTION

There is interest in the utilization of perfluorocarbons for lubricants,

containers, and binding materials because of their chemical stability relative to their hydrocarbon equivalents. The utilization of perfluorocarbons for systems at higher temperatures may be of particular interest. While many investigations have been made concerning the pyrolysis of hydrocarbons, less information is available on the perfluorocarbons.

Among the investigations of pyrolysis reactions of perfluorocarbons that have been reported, there are four that are of particular interest. Teflon has been heated to about 600° C at both low and moderate pressures (ref. 1). The main product was perfluoroethylene when Teflon was heated at about 5 millimeters of mercury. When the pressure was allowed to increase to about 100 millimeters of mercury, some perfluorocyclobutane and perfluoropropene were also produced. Perfluoroethylene and a small quantity of perfluoropropene were produced from the thermal decomposition of perfluorocyclobutane at 360° to 560° C (ref. 2). Perfluoroisobutene was heated to 700° C to produce perfluoroethane and a high-molecular-weight fluorocarbon (ref. 3). Finally, perfluoropropane and perfluoroethane were decomposed by means of a heated platinum filament (between 1000° and 1400° C) in a cooled vessel (ref. 4). The perfluoropropane produced perfluoroethane, a small quantity of perfluoropropene, some perfluoroisobutene, and polymeric solids. The perfluoroethane produced carbon tetrafluoride and a polymeric solid. In addition to the products, reference 4 gives some rate data for the decomposition of perfluoropropane and perfluoroethane at the hot filament.

The procedure by which gases are heated at a hot filament (in a cooled vessel) involves a nonuniform pyrolysis environment with large temperature gradients in the gas phase. As a result, for comparable reaction rates, some of the gas phase would be heated to a higher temperature than if the gases were heated at the vessel wall. In addition, the cooled walls may quench the decomposition reaction more rapidly. The reaction rates for the decomposition of perfluoropropane and perfluoroethane at the heated platinum filament may, therefore, differ from the decomposition rates under a more uniform heating environment. Furthermore, the courses of the reaction may even differ for the two procedures.

The present investigation was concerned with the pyrolysis reactions of three linear perfluorocarbons, which may be considered as representative of all linear perfluoroalkanes, in a wall-heated Inconel bomb: (1) carbon tetrafluoride (only carbon-fluorine bonding), (2) perfluoroethane (two perfluoromethyl groups), and (3) perfluoropropane (two perfluoromethyl end groups attached to a perfluoromethylene group). The courses of the pyrolysis reactions of the perfluorocarbon gases were followed between 663° and 1090° C. In addition, some data were obtained for the rates of the pyrolysis reactions.

EXPERIMENTAL MATERIALS AND PROCEDURE

Materials

Perfluoropropane and carbon tetrafluoride. - Both gaseous perfluoropropane (boiling point, -36.7° C) and carbon tetrafluoride were obtained from commercial sources and were used without purification, since a comparison of their infrared spectra with individual spectra of the impurities indicated better than 99-mole-percent purity.

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Perfluoroethane. - Gaseous perfluoroethane was prepared by heating perfluoropropane (at 250 to 300 mm Hg) to about 800° C in an Inconel bomb for about 20 minutes. The gaseous products were passed through a trap at -195° C and were distilled subsequently at -110° C. The crude perfluoroethane so produced was then reheated and repurified. A comparison of the infrared spectra of the final product with known spectra of the impurities indicated the presence in the final product of only perfluoroethane, 2.45 mole percent carbon tetrafluoride, 0.54 mole percent perfluoropropane, and 0.23 mole percent silicon tetrafluoride. Molecular-weight determinations agreed with the value of 96.8 mole percent perfluoroethane obtained by subtraction.

Pyrolysis of Perfluorocarbons

Apparatus. - All pyrolysis reactions were run by the static method in an Inconel bomb (646 ml) that was heated in a wire-wound 210-volt furnace. The furnace temperature was held constant to within an estimated ±3° C. The bomb was connected to a Pyrex vacuum train for the usual gas manipulations by means of a small entry line (estimated volume, 10 ml) with a metal-to-glass connector.

Procedure. - Several perfluoropropane pyrolysis runs were initially made at about 800° C for the purpose of conditioning the bomb surface. In addition, prior to each pyrolysis run, the bomb was heated to about 900° C in vacuum for at least 15 minutes and then to the desired pyrolysis temperature for 15 minutes with a pressure of about 10^{-3} millimeter of mercury.

In order to minimize any effects that might result from different initial pressures, all tests were made at the same initial gas pressure. Gaseous nitrogen had been used to determine the pressures of the gas in the calibrated bulb that were required to give a pressure of 100 millimeters of mercury after expansion into the heated bomb. The gas for pyrolysis was placed in the calibrated bulb at the desired pressure. Since pressure, temperature, and volume of the perfluorocarbon gas were known, the amount of the gas contained in the calibrated bulb was readily calculated from the ideal gas relation. Then, the gas was expanded into the heated bomb. Since it was found (with gaseous nitrogen) that a 30-second interval was more than sufficient to heat the gas within the bomb to the desired temperature, the bomb was opened briefly after 30 seconds to equalize the pressure within the bomb, bulb, and manometer system. The bomb valve was closed, and the gas pressure observed. The amount of the perfluorocarbon gas remaining in the bulb and manometer system, after expansion into the bomb, was calculated. The amount of gaseous perfluorocarbon that had been introduced into the bomb for the pyrolysis reaction, therefore, was readily determined by subtraction. All gaseous materials remaining in the bulb and manometer system were evacuated.

After the desired time interval, the pyrolysis reaction was quenched rapidly by trapping all the gaseous materials remaining in the bomb at -195° C. The total amount of the gaseous pyrolysis products was then calculated.

Analyses of the pyrolysis-product mixtures were obtained from comparisons of the infrared spectra of these mixtures with standardized spectra. Standardized

infrared-spectra curves had been obtained by plotting the reciprocal of the transmittance of an absorption peak against the respective gas pressure for pure gaseous carbon tetrafluoride, perfluoroethane, perfluoropropane, perfluoroisobutene, and silicon tetrafluoride. The absorption peaks used for the curves were those for which there would be negligible absorption contributions from the other gases and those that would be almost linear over the pressure range of interest. The percentage of each gaseous product, therefore, was determined from quantitative comparisons of the infrared spectra of the gaseous pyrolysis mixtures with the standardized infrared spectra curves of the pure materials.

For an investigation of possible heterogeneous effects on the pyrolysis of these perfluorocarbons, the surface-volume ratio was almost doubled by the addition of fine nickel wire (about 0.02-in. diam.).

RESULTS AND DISCUSSION

Perfluoropropane

Several 15-minute pyrolysis runs were made with perfluoropropane (C_3F_8) (at an initial pressure of 100 mm Hg) in the Inconel bomb between 663° and 1033° C. The amounts of the gaseous reactants and products (including unreacted perfluoropropane) are shown in table I(a). The number of moles of these gaseous materials obtained per mole of initial perfluoropropane is shown in figure 1.
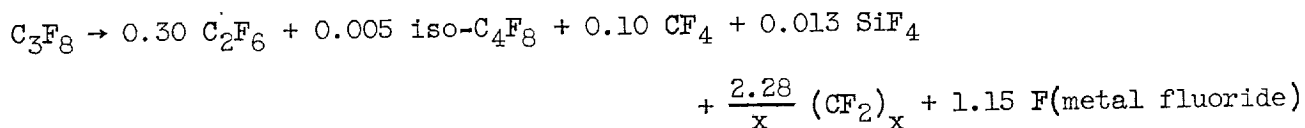
It was found that the gaseous products, up to about 750° C, were perfluoroethane (C_2F_6), some perfluoroisobutene (C_4F_8), a trace of perfluoropropene (C_3F_6), and unreacted perfluoropropane. The carbon that remained unaccounted for by these gaseous products was assumed to exist as a nonvolatile polymeric fluorocarbon, $(CF_2)_x$. The difference between the total amounts of fluorine and the amount accounted for by the assumed polymer and the gaseous products was assumed to exist as a metal fluoride. It was found that metal fluoride did volatilize and condense into the cold zone. This condensate was shown, by means of spot tests and X-ray diffraction, to contain nickel fluoride and iron compounds. A material balance at 713° C after the 15-minute interval indicated that essentially 1 mole of perfluoroethane was obtained per mole of perfluoropropane decomposed:

$$C_3F_8 \rightarrow 0.96\ C_2F_6 + 0.06\ \text{iso-}C_4F_8 + \frac{0.84}{x}\left(CF_2\right)_x + 0.08\ F(\text{metal fluoride})$$
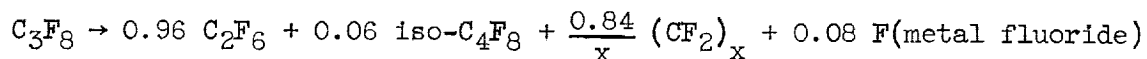
Reference 4 suggests a similar reaction course in which 1 mole of perfluoropropane decomposes essentially to 1 mole of perfluoroethane and some perfluoropropene, perfluoroisobutene, and polymeric fluorocarbon.

From about 750° C, the gaseous products (perfluoroethane and perfluoroisobutene) produced from the pyrolysis of perfluoropropane were being pyrolyzed subsequently to produce some carbon tetrafluoride (CF_4). In addition, small quantities of silicon tetrafluoride (SiF_4) were obtained. It is believed that this silicon tetrafluoride was produced primarily by a reaction between the pyrolysis products and the small Pyrex connector between the vacuum train and the Inconel

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bomb. A material balance at 861° C after the 15-minute interval indicated that the major products were the assumed nonvolatile polymeric fluorocarbon and the metal fluoride:

$$C_3F_8 \rightarrow 0.30 \; C_2F_6 + 0.005 \; iso\text{-}C_4F_8 + 0.10 \; CF_4 + 0.013 \; SiF_4$$

$$+ \frac{2.28}{x} (CF_2)_x + 1.15 \; F(\text{metal fluoride})$$

Finally, at about 930° C, the carbon tetrafluoride, produced as a relatively minor constituent in the subsequent pyrolysis of the perfluoroethane product, was in turn decomposed to nongaseous products.

Some rate data were obtained for the pyrolysis reaction of perfluoropropane in the Inconel bomb between 670° and 719° C. (All initial gas pressures were about 100 mm Hg.) A first-order reaction was assumed for the disappearance of perfluoropropane. A plot of the logarithm of the mole fraction of the remaining perfluoropropane against time is shown in figure 2. Values of the specific reaction-rate constant k, which were calculated from the first-order equations, are shown in table II(a).

As suggested by the Arrhenius equation, these specific rate constants were plotted against the reciprocal of the absolute temperature. The rate equation for the pyrolysis of perfluoropropane was calculated to be

$$k = 2 \times 10^{14} e^{-80,000/RT} \qquad (\text{sec}^{-1})$$

where R is the universal gas constant and T is temperature.

In reference 4 it is reported that the much higher temperature range of 1000° to 1200° C was required for the decomposition of perfluoropropane at the hot filament. Thus, a slower rate for the decomposition is indicated. As evidence for this decreased reactivity, the rate equation calculated from the data presented in reference 4 is as follows:

$$k = 7.5 \times 10^8 e^{-84,000/RT} \qquad (\text{sec}^{-1})$$

Perfluoroethane

By a procedure similar to that used for perfluoropropane, several 15-minute pyrolysis runs were made with perfluoroethane between 746° and 990° C. The amounts of the gaseous reactants and products (including unreacted perfluoroethane) are shown in table I(b). The number of moles of the gaseous materials obtained per mole of initial perfluoroethane is shown in figure 3.

As had been assumed for perfluoropropane, the amount of carbon that remained unaccounted for by the gaseous products of the pyrolysis of perfluoroethane was assumed to exist as a nonvolatile polymeric fluorocarbon, $(CF_2)_x$. The fluorine that remained unaccounted for by the assumed polymer or the gaseous products was

assumed to exist as a metal fluoride. A material balance was made at 824° C after the 15-minute pyrolysis interval. Analyses indicated that about 4 moles of fluorine, as a polymeric fluorocarbon, $(CF_2)_x$, and 2 moles of fluorine, as a metal fluoride, were obtained per mole of decomposed perfluoroethane:

$$C_2F_6 + metal(Inconel) \rightarrow \frac{1.95}{x} (CF_2)_x + 1.87\ F(metal\ fluoride)$$

$$+ 0.05\ CF_4 + 0.007\ SiF_4$$
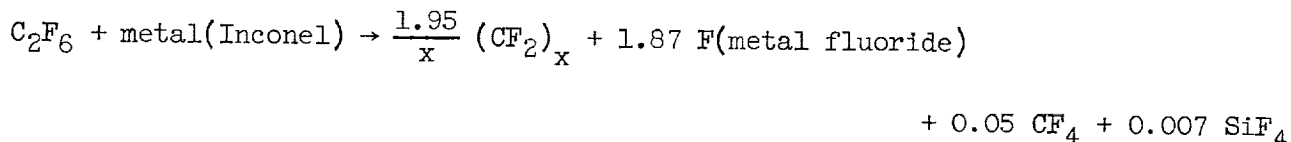
Although relatively slow at about 830° C, the rate of the formation of carbon tetrafluoride did increase somewhat with temperature. For example, at about 930° C, 0.25 mole of carbon tetrafluoride was formed per mole of perfluoroethane decomposed. At about 930° C, however, the carbon tetrafluoride was subsequently decomposed to only the polymer and metal fluoride.

In reference 4 a somewhat different course is suggested for the pyrolysis of perfluoroethane. Apparently, the principal net reaction involved the formation of 1 mole of carbon tetrafluoride per mole of perfluoroethane pyrolyzed. Although the present investigation (as shown in fig. 3) did indicate that the quantity of carbon tetrafluoride increased somewhat with increasing temperature, nothing approaching a 1:1 molar conversion was ever obtained. For example, at 870° C, where essentially all the perfluoroethane had decomposed within the 15-minute interval, only about 11 percent had decomposed to produce carbon tetrafluoride.

An explanation for the somewhat different reaction courses for the pyrolyses of perfluoroethane is not obvious. It may have been that different conditions were involved in the decomposition of perfluoroethane at the hot platinum filament and in the homogeneous reaction: (1) decomposition may have occurred primarily at the filament, which was at a much higher temperature; and (2) as suggested in reference 4, decomposition at the filament may have been catalyzed by the platinum wire. Since the environmental conditions for the pyrolysis of perfluoroethane may have differed, the reaction courses could have differed also.

In a manner similar to that used for perfluoropropane, some rate data were obtained for the pyrolysis of perfluoroethane between 747° and 807° C. A first-order reaction was assumed for the disappearance of perfluoroethane. Values of the specific reaction-rate constant k, which were calculated from the first-order equations, are shown in table II(b).

An Arrhenius-type plot led to the calculation of the following rate equation for the pyrolysis of perfluoroethane:

$$k = 3 \times 10^7 e^{-53,000/RT} \qquad (sec^{-1})$$

In reference 5 a similar rate equation is given for the pyrolysis of perfluoroethane by means of the flowing-toluene procedure:

$$k = 10^8 e^{-50,000/RT} \qquad (sec^{-1})$$

Reference 4 observed a much slower reaction for the decomposition of perfluoroethane at the hot filament, however. First, a much higher temperature range of 1000° to 1400° C was necessary for the decomposition reaction; second, the slower reaction is shown by the rate equation that was calculated from the data of reference 4:

$$k = 2.1 \times 10^2 e^{-51,000/RT} \qquad (\text{sec}^{-1})$$

The major products for the pyrolysis of perfluoroethane up to about 830° C in the Inconel bomb were assumed to be a polymeric fluorocarbon and a metal fluoride. At first glance, the presence of a metal fluoride as a major product may seem to indicate that the decomposition of perfluoroethane involves a heterogeneous initiation. No increase in the reaction rate was observed, though, at 770° C with a twofold increase in the surface. It is believed, therefore, that the metal fluoride was formed by the subsequent reaction of fluorine, formed during the pyrolysis, with the metal walls rather than by the heterogeneous initiation of the pyrolysis reaction at the walls. In the case of ethane, it is generally believed that the pyrolysis of the hydrocarbon occurred by means of a chain mechanism with the formation of ethylene and hydrogen as major products. Perfluoroethane may also pyrolyze by means of a chain mechanism with the formation of fluorine. Because of its extreme reactivity, however, any fluorine so produced would readily form metal fluorides at the walls.

Carbon Tetrafluoride

In a manner similar to that used for perfluoropropane and perfluoroethane, several 15-minute pyrolysis runs were made with carbon tetrafluoride (100 mm Hg) in the Inconel bomb between 936° and 1090° C. The amounts of the gaseous reactants and products (including unreacted carbon tetrafluoride) are shown in table I(c). The number of moles of the unreacted carbon tetrafluoride obtained per mole of initial carbon tetrafluoride is shown in figure 4.

Since the only gaseous fluorocarbon obtained was unreacted carbon tetrafluoride, the products were assumed to be a nonvolatile polymeric fluorocarbon, $(CF_2)_x$, and a metal fluoride:
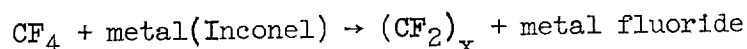
$$CF_4 + \text{metal(Inconel)} \rightarrow (CF_2)_x + \text{metal fluoride}$$

Some rate data were obtained for the pyrolysis of carbon tetrafluoride (100 mm Hg) in the Inconel bomb between 930° and 990° C. A first-order reaction for the disappearance of carbon tetrafluoride was assumed. Values of the specific reaction-rate constant k, which were calculated from the first-order equations, are shown in table II(c). From an Arrhenius-type plot, the rate equation for the pyrolysis of carbon tetrafluoride was calculated to be as follows:

$$k = 4 \times 10^{13} e^{-96,000/RT} \qquad (\text{sec}^{-1})$$

As discussed for perfluoroethane, the presence of a metal fluoride as a major product in the pyrolysis of carbon tetrafluoride is not necessarily indicative of a heterogeneous initiation. Instead, evidence was obtained to suggest

that the pyrolysis was homogeneous. First, the value of 4×10^{13} sec^{-1} calculated for the frequency factor agrees closely with values that are often observed for homogeneous reactions. Second, no increase in the reaction rate was observed at 990° C with a twofold increase in the surface.

SUMMARY OF RESULTS

The more significant results that were obtained from the pyrolysis of three linear perfluoroalkanes in an Inconel bomb were as follows:

1. Perfluoropropane, starting at about 660° C, was pyrolyzed essentially to perfluoroethane, some perfluoroisobutene, and a nonvolatile polymeric fluorocarbon. A rate equation for the pyrolysis of perfluoropropane between 670° and 719° C was given as follows:

$$k = 2 \times 10^{14} e^{-80,000/RT} \qquad (\text{sec}^{-1})$$

where k is the specific reaction-rate constant, R is the universal gas constant, and T is temperature.

2. Perfluoroethane, starting at about 750° C, was pyrolyzed essentially to nonvolatile products that must have been primarily a nonvolatile polymeric fluorocarbon and a metal fluoride. A secondary reaction, whose rate increased somewhat with increasing temperature, was responsible for the formation of some carbon tetrafluoride. A rate equation for the pyrolysis of perfluoroethane between 745° and 805° C was given as follows:

$$k = 3 \times 10^{7} e^{-53,000/RT} \qquad (\text{sec}^{-1})$$

3. Carbon tetrafluoride, starting at about 930° C, was pyrolyzed to nonvolatile products that must have been primarily a nonvolatile polymeric fluorocarbon and a metal fluoride. A rate equation for the pyrolysis between 930° and 990° C was given as follows:

$$k = 4 \times 10^{13} e^{-96,000/RT} \qquad (\text{sec}^{-1})$$

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    National Aeronautics and Space Administration
       Cleveland, Ohio, April 17, 1963

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TABLE I. - YIELD OF REACTANTS AND PRODUCTS FROM 15-MINUTE PYROLYSIS RUNS

[Concentrations in millimoles.]

(a) Perfluoropropane

Temperature, °C	Perfluoropropane		Perfluoroethane	Carbon tetrafluoride	Perfluoroisobutene	Perfluoropropene	Silicon tetrafluoride
	Initial	Unreacted					
663	0.895	[a]0.913	0.033	-----	trace	trace	-----
713	.885	.617	.257	-----	0.016	-----	-----
752	.860	.192	.562	-----	.115	-----	-----
787	.832	.057	.610	0.007	.051	-----	0.006
812	.835	.059	.542	.020	.057	-----	-----
837	.778	.031	.291	.038	.001	-----	.005
861	.787	.027	.225	.075	.004	-----	.010
885	.755	.011	.037	.127	-----	-----	.008
909	.765	.008	-----	.203	-----	-----	.008
957	.750	.008	.008	.233	-----	-----	.006
1033	.678	-----	-----	.008	-----	-----	.001

[a]Because of experimental difficulties encountered, a relatively large experimental error (estimated at about 4.6 percent) was observed for this point. The correct value is believed to be about 0.87 millimole.

(b) Perfluoroethane

Temperature, °C	Perfluoroethane		Carbon tetrafluoride	Silicon tetrafluoride
	Initial	Unreacted		
746	0.819	0.777	0.002	0.006
771	.821	.649	.008	.007
824	.739	.130	.029	.004
868	.743	.003	.085	.008
893	.743	.004	.127	.006
932	.770	.007	.210	.006
932	.737	.004	.191	.008
990	.700	.007	.142	.005
990	.690	.005	.146	.013

(c) Carbon tetrafluoride

Temperature, °C	Carbon tetrafluoride		Silicon tetrafluoride
	Initial	Unreacted	
936	0.747	0.702	0.003
990	.737	.318	.005
1040	.724	.009	.006
1090	.718	.002	.014

TABLE II. - SPECIFIC REACTION RATES FOR PYROLYSIS

(a) Perfluoropropane

Temperature, °C	Average reaction-rate constant, k, sec^{-1}
670	0.71×10^4
686	1.51
697	1.97
708	3.51
719	6.3

(b) Perfluoroethane

Temperature, °C	Average reaction-rate constant, k, sec^{-1}
747	1.30×10^4
763	2.12
774	2.49
785	3.05
807	6.2

(c) Carbon tetrafluoride

Temperature, °C	Average reaction-rate constant, k, sec^{-1}
930	1.37×10^4
936	2.09
950	2.34
958	3.90
968	4.77
990	9.3

11
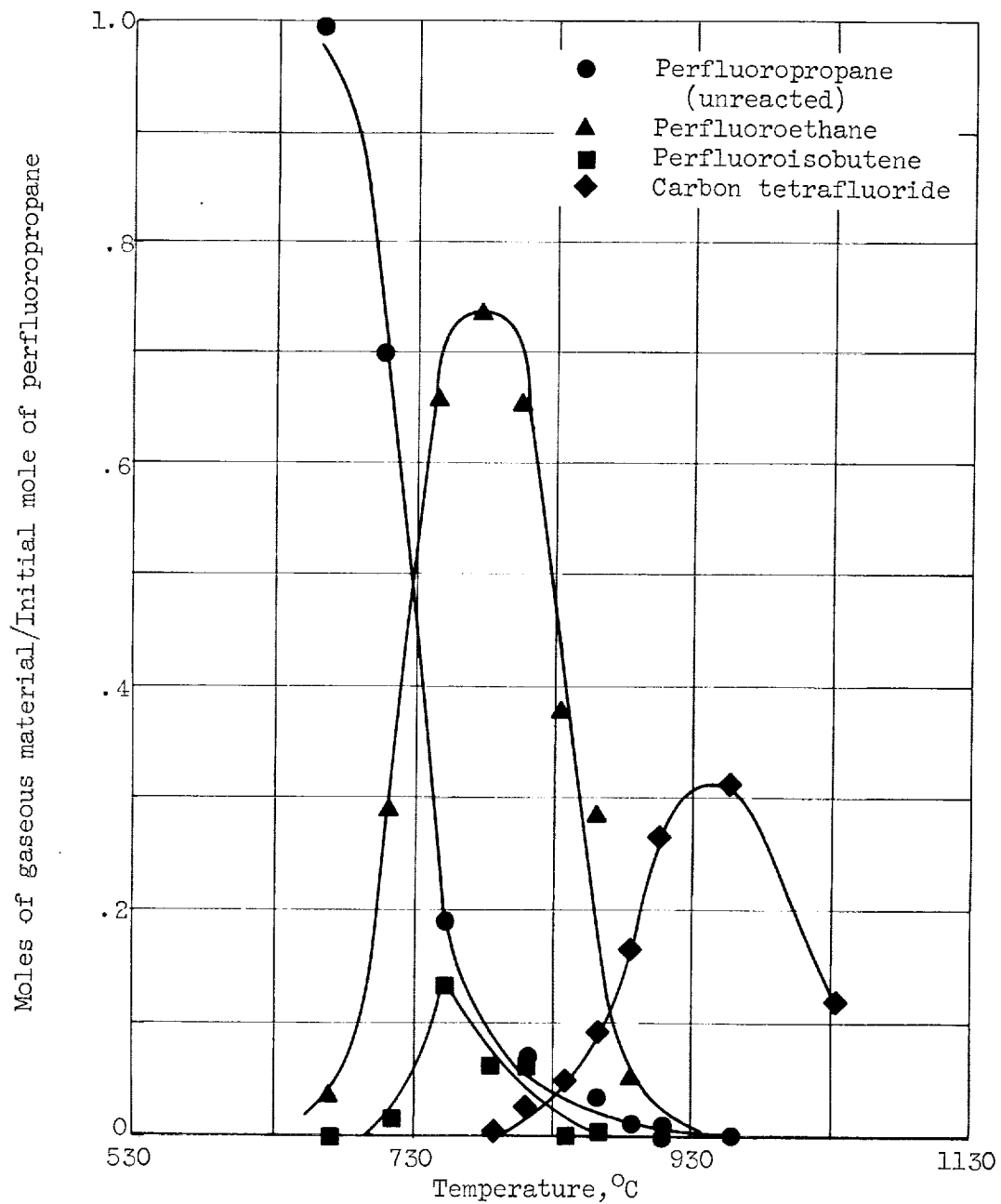
Figure 1. - Composition of gas after pyrolysis of per-
fluoropropane. Time, 15 minutes; initial pressure,
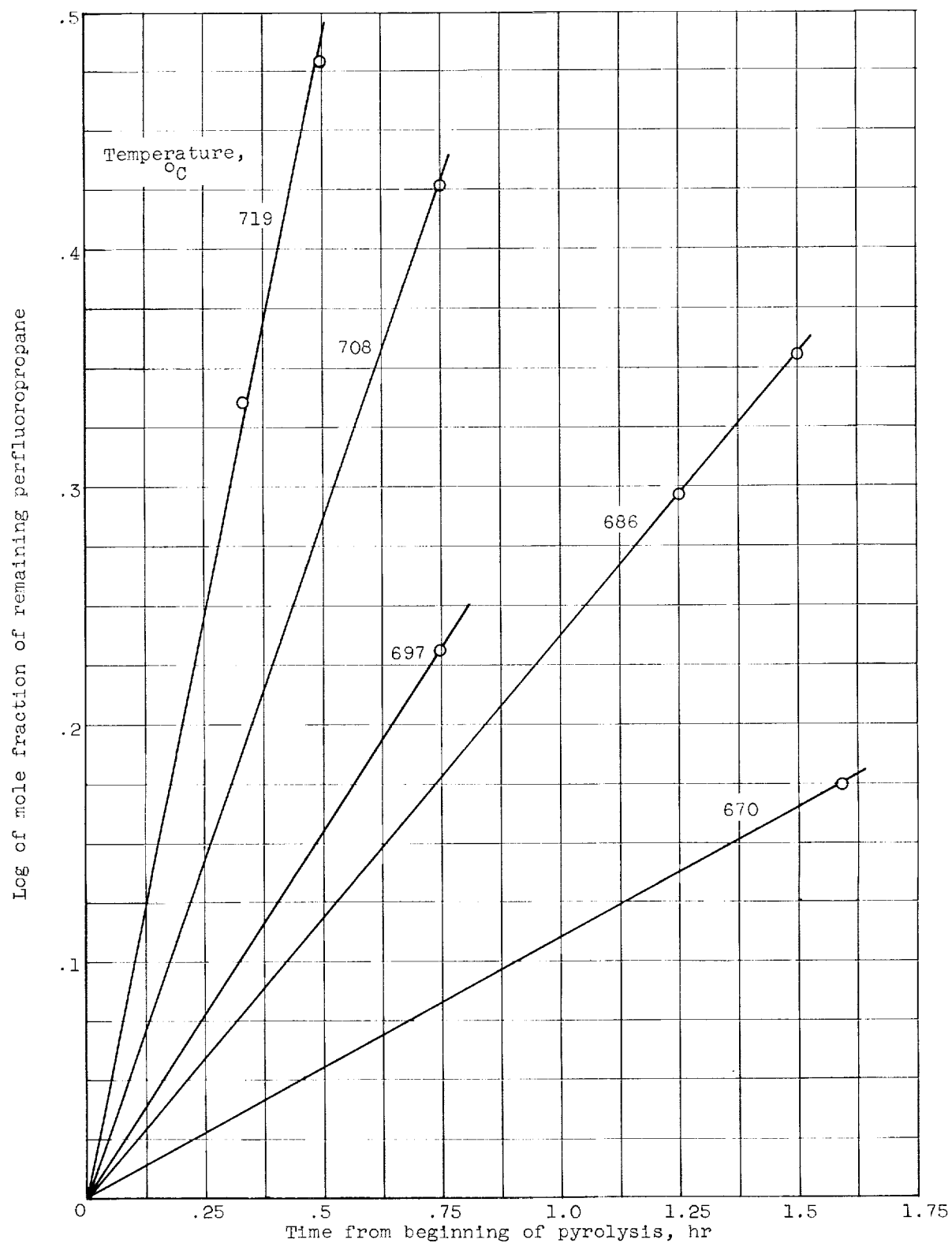100 millimeters of mercury.

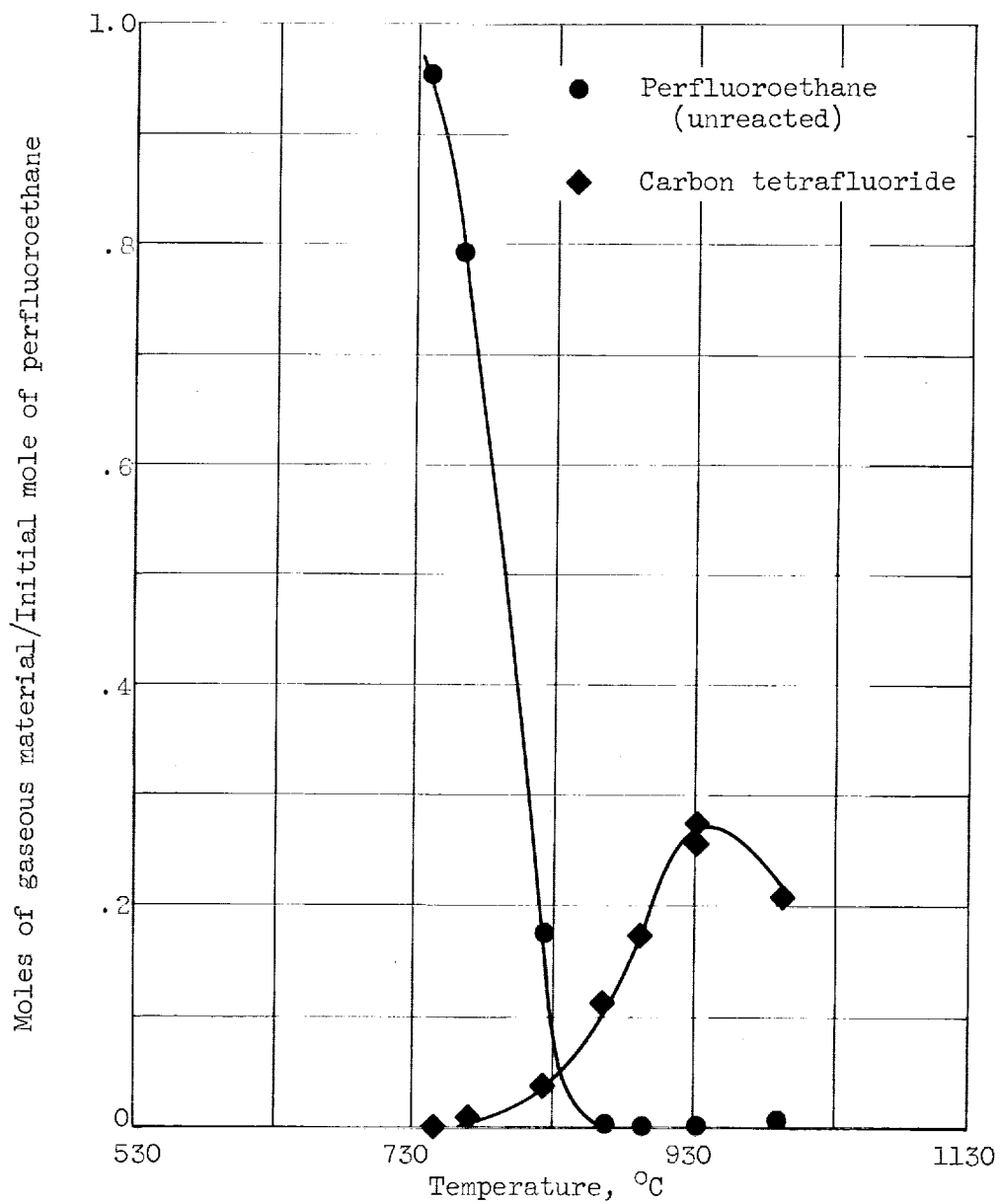Figure 2. - Fraction of perfluoropropane during assumed first-order pyrolysis reaction.

Figure 3. - Composition of gas after pyrolysis of perfluoroethane. Time, 15 minutes; initial pressure, 100 millimeters of mercury.
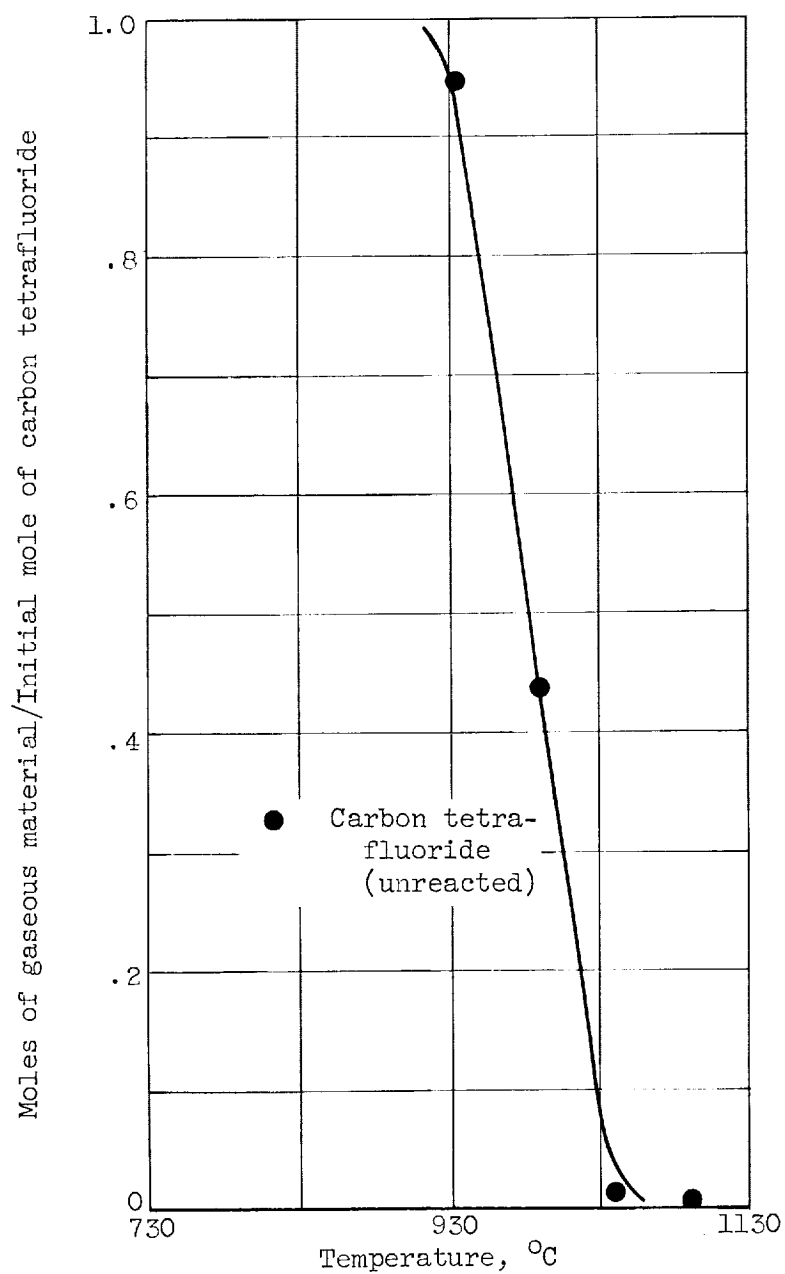
Figure 4. - Composition of gas after pyrolysis of carbon tetrafluoride. Time, 15 minutes; initial pressure, 100 millimeters of mercury.